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Piloted Ignition to Flaming in Smoldering Fire-Retarded Polyurethane Foam

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Experimental results are presented on the piloted transition from smoldering to flaming in the fire-retarded polyurethane foam Pyrell[®]. The samples are small rectangular blocks with a square cross section, vertically placed in the wall of a vertical wind tunnel. Three of the vertical sample sides are insulated and the fourth side is exposed to an upward oxidizer flow of variable oxygen concentration and to a variable radiant heat flux. The gases emitted from the smoldering reaction pass upwards through a pilot, which consists of a coiled resistance heating wire. In order to compensate for the solid-phase and gas-phase effects of the fire retardants on the piloted transition from smoldering to flaming in Pyrell, it was necessary to assist the process by increasing the power supplied to the smolder igniter and the pilot (compared to that used for non-fire retarded foam). The experiments indicate that the piloted transition from smoldering to flaming occurs when the gaseous mixture at the pilot passes the lean flammability limit. It was found that increasing the oxygen concentration or the external heat flux increases the likelihood of a piloted transition from smoldering to flaming, and generally decreases the time delay to transition. The piloted transition to flaming is observed in oxygen concentrations of 23% and above in both low-density and high-density Pyrell. Comparisons with previous experiments show that the piloted transition from smoldering to flaming is possible under a wider range of external conditions (i.e. lower oxygen concentration) than the spontaneous transition from smoldering to flaming. The results show that the fire retardants in Pyrell are very effective in preventing the piloted transition to flaming in normal air, but Pyrell is susceptible to smoldering and the piloted transition to flaming in oxygen-enriched environments. Therefore, precautions should be taken in the design of applications of Pyrell in oxygen-enriched environments to reduce to the risk of a piloted transition to flaming.

1. Introduction

Smoldering is a slowly propagating, low temperature, heterogeneous combustion reaction in which oxygen directly attacks the surface of a fuel [1]. Porous, open-celled materials such as flexible polyurethane foam are especially well suited to support smoldering due to their high surface area per unit volume, self-insulating properties, and permeability for oxidizer transport. From a fire safety perspective, smoldering is a significant concern, as 25% of residential fire deaths in the United States are caused by fires originating from smoldering smoking materials.[2] A smolder reaction can be initiated by a heat source too weak to directly produce a flaming reaction [3-5] and releases toxic and flammable gases such as carbon monoxide, pyrolysates and large oxygenated molecules [6,7]. Several works have studied the spontaneous transition from

smoldering to flaming, whereby the smolder reaction supplies the gaseous fuel and heat to trigger a gas-phase ignition [8-10]. However, very little work has been done on the piloted ignition of the gaseous products of smoldering [11]. This scenario presents another significant fire risk because the smolder product gases could be ignited by a spark or high-temperature heat source in the vicinity of the smoldering material. In addition, the piloted transition from smoldering to flaming could be possible under a wider range of external conditions (oxygen concentrations, oxidizer flow velocities, and external heat fluxes) than the spontaneous transition from smoldering to flaming.

There are several test methods currently used to assess the flammability of materials, such as the Cone Calorimeter [12], the LIFT apparatus [13], and the Fire Propagation Apparatus [14]. These methods allow the determination of the critical (minimum) heat flux for ignition for a given material, by using a pilot to ignite the pyrolysis vapors emanating from a radiatively heated solid. However, these methods are not designed to initiate a smolder reaction in a sample, and therefore have to be adapted to test the piloted transition from smoldering to flaming. The current study seeks to investigate this problem and help fill the gap in flammability testing of porous materials.

The material chosen for this study is Pyrell^{®*}, a combustion modified (fire retarded) polyurethane foam that is currently one of the allowed materials for equipment stowage protection in the NASA Space Shuttles and the International Space Station [15]. However, for future extended space flights, NASA is considering using higher spacecraft oxygen concentrations in order to lower the total pressure (by reducing the nitrogen partial pressure) [16]. The benefits of reducing the total cabin pressure include minimizing weight and facilitating extra vehicular activity (EVA) by reducing the risk of decompression sickness. In a recent NASA report [17], the Exploration Atmospheres Working Group has recommended that the lunar and Mars landers and surface habitats operate at 32% oxygen and 8.0 psia. In practice, there are fluctuations around the nominal oxygen concentration; for the Mars mission the control range is expected to be +/- 2%. Clearly, the flammability of Pyrell in elevated oxygen concentrations must be examined. The present study investigates the piloted transition from smoldering to flaming in Pyrell in oxygen-enriched environments.

Putzeys et al. [18] conducted a study on the piloted transition from smoldering to flaming in non-fire retarded (NFR) flexible polyurethane foam of density 26.5 kg/m³, using the same experimental apparatus as that in the present study. The NFR foam was found to undergo a piloted transition from smoldering to flaming in oxygen mole fractions as low as 0.17. In addition, the experimental results indicated that piloted transition to flaming was dependent on the gaseous mixture passing the lean flammability limit, and the critical pyrolysis mass production rate for the transition to flaming was determined.

To date, there has been very little work published on the flammability of Pyrell foam. Putzeys et al. [19] investigated the spontaneous (unpiloted) transition from smoldering to flaming in Pyrell. It was found that Pyrell undergoes a weak smoldering reaction that requires significant assistance in the form of external heating and elevated oxygen concentrations. The spontaneous transition to flaming was observed in high-density Pyrell at oxygen mole fractions of 0.35 and above, and in low-density Pyrell at oxygen mole fractions of 0.40 and above.

* Pyrell[®] is a registered trademark of Foamex International, Inc., Linwood, PA, USA. Commercial trade names are used for certain products in this report for identification purposes. This use does not constitute an endorsement by UC Berkeley or the US Government.

Hshieh et al. showed that in 30% oxygen and 70.3 kPa, Pyrell fails the NASA Upward Flame Propagation Test (NASA STD-6001 Test 1) because the flame spreads up the entire sample length. Hshieh et al. also subjected Pyrell to cone calorimeter experiments in 21% oxygen, and found that the minimum heat flux for ignition (by spark igniter) was 27 kW/m². When exposed to a radiant heat flux of 26 kW/m² for 10 minutes in the cone calorimeter, Pyrell smoldered, but the smolder reaction quickly extinguished upon removal of the external heat source [15].

Levchik and Weil compiled a comprehensive review of the many types of fire retardants currently used in flexible polyurethane foams [20]. The most common fire retardants are phosphorus-containing additives and halogen-phosphorus-containing additives. The most widely used commercial fire retardant is the halogen-phosphorus-containing compound TDCPP, which acts in both the condensed and vapor phases. In the solid phase, a phosphorus-containing carbonaceous layer grows between the flame and the pyrolysis zone, and acts as a barrier for the transfer of heat and fuel [21]. In the gas phase, the vaporized TDCPP dilutes the fuel vapors to reduce the fuel oxidation reaction rates, therefore hindering gas-phase ignition and flaming [22]. Halogen-phosphorus-containing additives also inhibit ignition and flaming by radical scavenging: the decomposition of halogen-phosphorus additives produces both halogen radicals and phosphorus compound radicals that scavenge OH* and H* radicals, which can otherwise react in highly exothermic flaming [23]. Jayakody et al. tested a wide variety of commercial fire retardants in polyurethane foam using a cone calorimeter, and found that TDCPP was the most effective and reduced the peak heat release rate by 21% [24].

Another common fire retardant, melamine, is usually synergistic with phosphorus or halogen-phosphorus additives, and is especially useful in suppressing smoldering [20]. Bastin et al. suggested that the synergistic effect is that the TDCPP generates phosphoric acid, which promotes the conversion of melamine into thermally stable network structures such as melam, melem, and melone [25]. Dick et al. used ¹H NMR spectroscopy to find that the melamine additive acts in the condensed phase by promoting the formation of a rigid char at temperatures above 400°C [26]. Melamine is also believed to act as a heat sink, and the nitrogen content of melamine may partly end up as nitrogen gas, providing a heat sink and diluent in the gas phase [27]. In addition, the melamine is believed to react with the evolved toluene diisocyanate fraction arising from the decomposition of polyurethane, to form a polymeric structure that reduces the smoke and CO release [27].

2. Experiment

2.1. Experimental Concept and Background

The current study is part of a NASA-sponsored program to study the transition from smoldering to flaming in environmental conditions encountered in spacecraft facilities, i.e. microgravity, low velocity gas flows of varied oxygen concentrations. The microgravity experiments were initially planned for the International Space Station, and therefore the sample size had to be limited for safety and launch mass reasons, to dimensions of 50 x 50 x 125 mm. The small dimensions of the sample make it quite difficult to achieve a self-sustaining smolder reaction. Smoldering is a weak reaction whose propagation is dictated by a balance between the heat generated at the smolder reaction and the heat transferred ahead of the smolder front and lost to the surroundings. The heat losses are proportional to the surface area of the sample, while the heat generation is

proportional to the volume of the sample. Therefore, as the sample size is decreased, the ratio of heat losses to heat generation increases. It was found in previous testing that in order to achieve a propagating smolder reaction in the current small samples, the heat losses had to be reduced with external heating in the form of guard heaters and a radiant heat flux [10].

The experimental setup is a modification of that previously used to study the spontaneous transition from smoldering to flaming [10,19,28]. It consists of a vertically oriented parallelepiped foam sample heated on three of its surfaces with guard heaters (maintained at 200 °C) and with the fourth, free surface, exposed to a parallel forced oxidizer flow and radiant heat flux (Fig. 1). Smolder is initiated at the bottom of the sample and the smolder reaction propagates upward in the same direction as the oxidizer flow (buoyant and forced), i.e., forward smoldering. The gases emitted from the smoldering sample mix with the duct oxidizer flow and travel upwards through the pilot. When the gas mixture at the pilot is flammable, the gases may ignite. If the gas-phase reaction is sufficiently strong, the flame will propagate upstream and engulf the sample.

2.2. Apparatus

The experiments are conducted in a small vertically oriented aluminum flow duct (Fig. 1), 380 mm long and with a cross-sectional area of 135 mm by 80 mm. Two walls of the flow duct consist of panes of borosilicate glass for optical access for a video camera and a high-speed camera (Kodak Ektapro[®] Model 2000). The oxidizer flow entering the test section of the flow duct first passes through a settling chamber and a converging nozzle.

The sample holder is constructed of thin-walled (0.75 mm) brass sheets insulated with Fiberfrax[™], with a central cavity to contain the fuel sample (50 mm x 50 mm cross section and 125 mm long), and the igniter holder assembly. The outer surfaces of the back and side walls of the sample holder each have a guard heater independently controlled by a Minco[®] temperature controller.

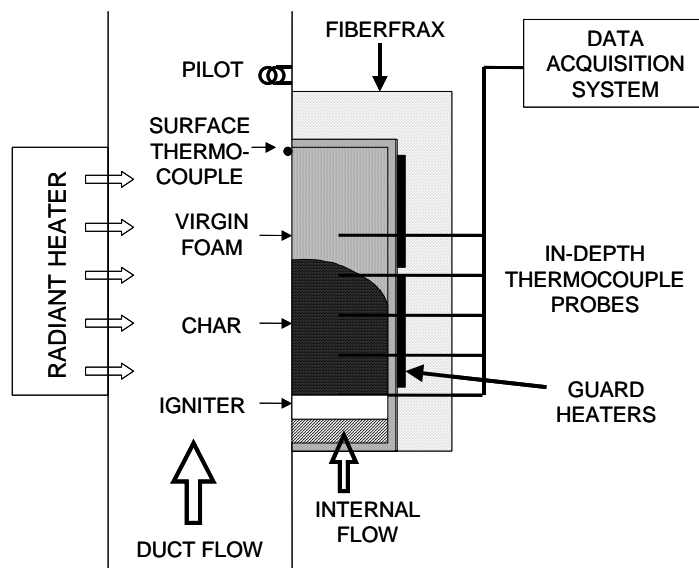


Figure 1: Schematic of the apparatus

An infrared radiant strip heater (Research Inc. Model 4184) is mounted opposite the sample holder in the vertical wall of the flow duct to counter heat losses from the free surface of the fuel sample with a radiant flux perpendicular to the sample surface.

In order to initiate the smolder reaction, the bottom face of the sample is in contact with an electrically heated ceramic honeycomb igniter of area 50 mm by 50 mm. During the tests, the igniter is supplied with a power of 115 W. The bottom face of the igniter is insulated with a layer of Fiberfrax™ of thickness 15 mm. During the tests, there is a forced flow of oxidizer through the Fiberfrax™ and the igniter, and into the fuel sample at a flow rate of 13.4 cc/s, which was determined to be the optimal internal flow rate for smolder initiation and propagation from previous testing.

The duct oxidizer flow, set to 0.15 m/s for all tests, is controlled using two identical sets of critical flow nozzles. The internal oxidizer flow through the igniter is controlled using mass flow controllers. Oxygen is added to air to achieve the enriched oxygen concentrations, and nitrogen is added to air to achieve sub-atmospheric oxygen concentrations.

The pilot consists of a coiled Nichrome (80% Nickel/ 20% Chromium) wire with a resistance of 5.27 ohms/m. The entire coil is 45 mm long and consists of seven coils of 7 mm diameter. The pilot's axis is located 15 mm downstream from the top edge of the fuel sample and 5 mm from the flow duct wall. The pilot covers the entire species boundary layer, in order to remove the pilot's transverse location as a parameter of the problem. The vertical location of the pilot was chosen to be as close to the sample as possible while providing negligible direct heating to the sample. The pilot is supplied with 10 A of current from a DC power supply.

As shown in Fig. 1, five type-K thermocouples are located along the centerline of the sample at distances from the igniter/fuel interface of: 0, 20, 40, 60, and 80 mm. The thermocouples are 0.84 mm diameter sheathed grounded probes, inserted through the back of the sample. In addition, there is a bare thermocouple placed at the top of the front sample surface, in order to detect the ignition event as it occurs.

2.3. Pyrell Foam Samples

Tests were performed on the two commercially available densities of Pyrell: high-density (64.0 kg/m³) and low-density (35.3 kg/m³). Both foams achieved the top rating of HF-1 for the UL-94 flame resistance test. An Environmental Scanning Electron Microscope (ESEM) was used to take images of the cell structure of the virgin foams; examples are shown in Fig. 2(a) and (b). The images show the similarity in pore sizes between the two foams, and reveal that the high-density Pyrell has noticeably thicker solid strands, more surface area per unit volume, and smaller holes in the polyhedron faces than the low-density Pyrell. The average solid strand thicknesses of the high-density and low-density Pyrell, measured from the ESEM images, are approximately 102 μm and 61 μm, respectively. Since the total solid surface area per unit volume of foam is roughly proportional to the average solid strand thickness, it can be estimated that the high-density Pyrell has approximately 67% more solid surface area than the low-density Pyrell.

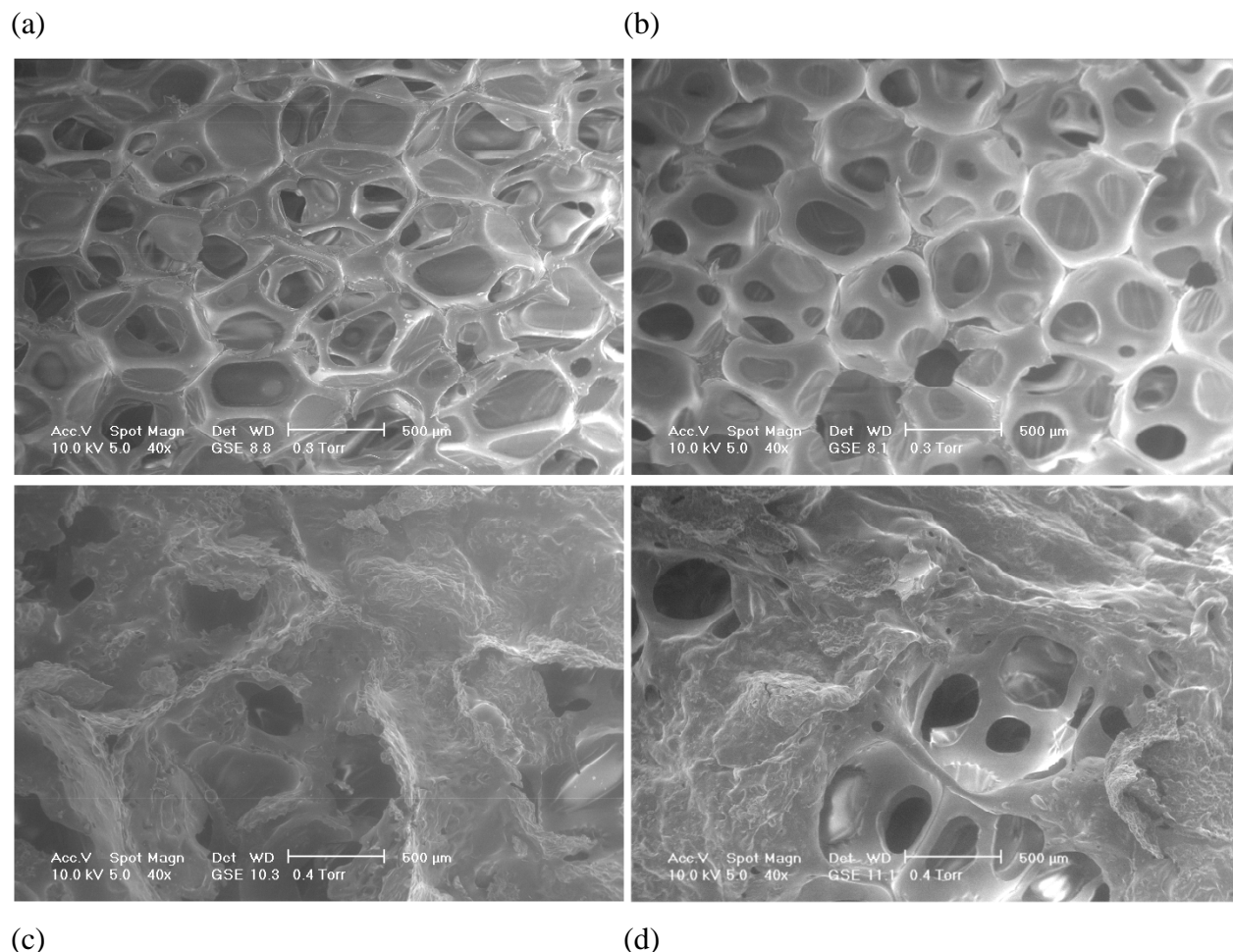


Figure 2: Environmental Scanning Electron Microscope (ESEM) images of (a) virgin low-density Pyrell and (b) virgin high-density Pyrell; and after application of a flame, (c) intumesced low-density Pyrell and (d) intumesced high-density Pyrell.

The Foamex Technical Products catalog describes the flame-resistant behavior of Pyrell in air: “When flame is applied, Pyrell intumesces. The surface chars, tending to form a protective shield between the flame and the foam underneath. This carbon char has low thermal conductivity and high oxidation resistance” [29]. The intumescent behavior of Pyrell can be seen in Fig. 2 (c) and (d): ESEM images of a surface of low-density and high-density Pyrell after being exposed to a direct flame. The images show that the most of the foam surface has intumesced and has lost its uniform cell-structure. Foamex does not provide data on the type or amount of fire retardants used in Pyrell because that information is proprietary. However, the Material Safety Data Sheet (MSDS) for Foamex’s polyurethane foams states that their fire retarded foams may release hydrogen chloride, hydrogen bromide, hydrogen fluoride or phosphoric acid depending on the fire retardant additive [30]. Halogen-phosphorus additives are known to promote the growth of a phosphorus-containing carbonaceous layer between the flame and the pyrolysis zone, which acts as a barrier for the transfer of heat and fuel [21]; this describes exactly the behavior of Pyrell. It therefore seems likely that Pyrell includes halogen-phosphorus-containing fire retardants.

2.4. Experimental Variables and Procedure

Tests are conducted varying the external radiant heat flux and the oxygen concentration of the duct and internal flows. The radiant heat flux is either 4.5 or 5.5 kW/m². The higher radiant heat flux was found in preliminary testing to be the maximum heat flux that would not produce a pyrolysis reaction on the front surface of the sample. The purpose of the radiant heater is not to promote pyrolysis but to supply additional heat to the sample (simulating a larger sample or an external heat source) and counter the convective heat losses on the free surface. The lower heat flux was found to be the minimum heat flux at which the sample could achieve a sustained smolder reaction. The oxygen mole fraction is varied between 0.21 and 0.35, which covers the range of oxygen concentrations that are currently used in NASA spacecraft, as well as the higher oxygen concentrations being planned for use in future space missions.

At the beginning of each test, the duct and internal flows are set, the radiant heater is turned on, and the Minco[®] heater temperature controllers are set to a set-point of 200 °C. When the guard heaters reach their set-point temperature, the igniter and the pilot are activated. If piloted ignition occurs, the flame is extinguished with a jet of carbon dioxide. If the smolder reaction reaches the top of the sample without a piloted ignition event, the test is stopped.

3. Results

A sequence of images depicting a piloted transition from smoldering to flaming is shown in Fig. 3. The test conditions were 0.25 oxygen mole fraction and 4.5 kW/m² radiant heat flux. The smolder front has propagated through approximately 30% of the sample height prior to the first image. The first image shows the pyrolysate (pyrolysis gases) passing upwards through the pilot. In the second image, the pyrolysate is no longer visible above the pilot, and a bright flame is seen directly underneath the pilot, indicating that the gases have been ignited by the pilot. In the third through seventh images, the flame is seen to propagate downwards, or upstream towards the source of gaseous fuel (the smolder front). In the last four images, the flame is seen to attach to the foam sample near the smolder front, and then spread over the entire sample.



Figure 3: Photographic sequence of a piloted transition from smoldering to flaming. Test conditions were 0.25 oxygen mole fraction and 4.5 kW/m² radiant heat flux.

Fig. 4 shows the thermocouple temperature history of the test displayed in Fig. 3. This data represents a characteristic temperature history of a test that underwent piloted transition to flaming. The temperature at the igniter/fuel interface (0 mm) begins to rise when the igniter is activated at 286 s. The temperature increase at 20 mm and 40 mm shows the upwards propagation of the smolder front in the sample. At 465 s, the surface thermocouple registers a drastic jump in temperature, indicating that the piloted ignition of smolder gases has occurred. The interior thermocouples do not reach typical flame temperatures because they are shielded from the flame's radiation by the foam and char, and the flame is quickly extinguished with a jet of carbon dioxide.

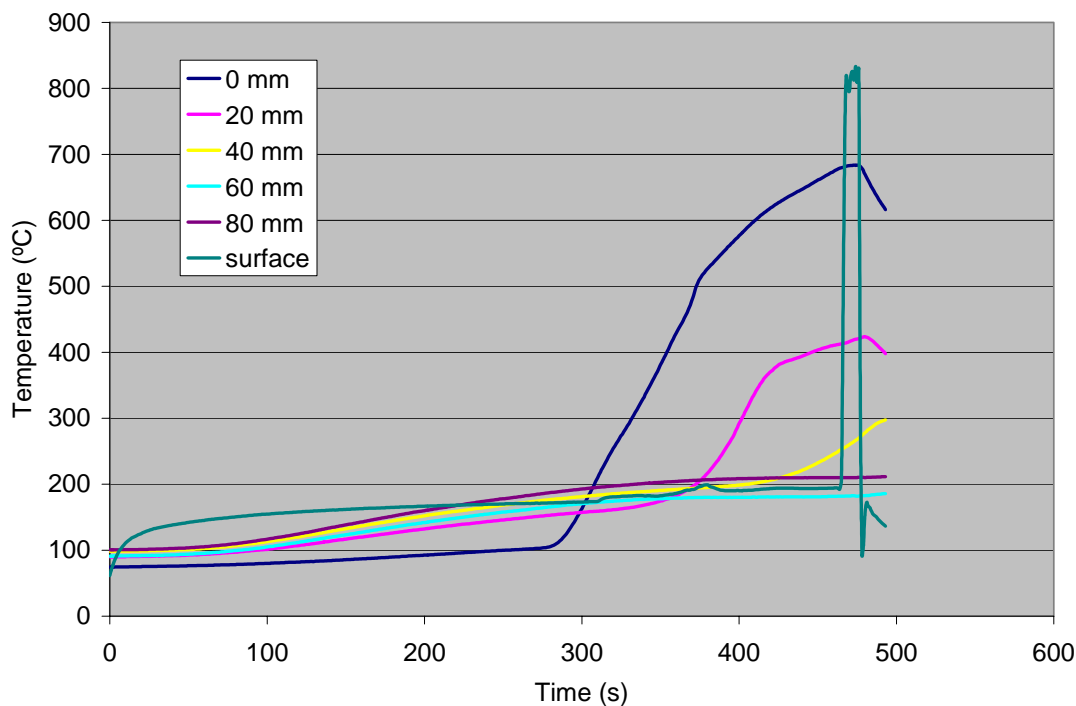


Figure 4: Temperature history of smoldering and piloted transition to flaming. Test conditions were 0.25 oxygen mole fraction and 4.5 kW/m² radiant heat flux. The heights in the legend indicate the height above the fuel/igniter interface. The “surface” thermocouple is located at the top of the front surface of the sample.

A series of tests was run at varying oxygen concentration and radiant heat flux. The results of these tests, in terms of whether or not a piloted transition to flaming occurred, are shown in Table 1. In addition, for the tests that underwent a transition to flaming, the time delay between the activation of the igniter and the transition to flaming is indicated. Table 1 shows that high-density and low-density Pyrell exhibited similar behavior in terms of the threshold values of oxygen concentration and radiant heat flux for the transition to flaming. All the tests at 0.25 oxygen mole fraction and above underwent transition to flaming, while none of the tests in normal air (0.21 oxygen mole fraction) underwent transition to flaming. At 0.23 oxygen mole fraction, only the tests at the higher radiant heat flux underwent transition to flaming. Because NASA is considering oxygen-enriched environments for future space missions, the finding that Pyrell is susceptible to a piloted transition to flaming in oxygen concentrations as low as 23% is cause for concern.

It can be seen from Table 1 that increasing the oxygen concentration or increasing the radiant heat flux generally decreases the time delay between igniter activation and the transition to flaming. Table 1 also shows that the time delays between the activation of the igniter and the transition to flaming are shorter for high-density Pyrell than for low-density Pyrell. Possible explanations for these differences will be discussed below.

Table 1: Test results for low-density and high-density Pyrell, for varying oxygen mole fraction and radiant heat flux. “Y” indicates a piloted transition to flaming, and “N” indicates no transition to flaming. The times indicate the time delay between the activation of the igniter and the transition to flaming event.

Oxygen Mole Fraction	Low-density Pyrell		High-density Pyrell	
	4.5 kW/m ²	5.5 kW/m ²	4.5 kW/m ²	5.5 kW/m ²
0.35	Y - 157 s	Y - 153 s	Y - 81 s	Y - 105 s
0.30	Y - 158 s	Y - 88 s	Y - 99 s	Y - 82 s
0.25	Y - 179 s	Y - 88 s	Y - 147 s	Y - 84 s
0.23	N	Y - 149 s	N	Y - 125 s
0.21	N	N	N	N

4. Discussion

The present study on the piloted transition to flaming of a smoldering material can benefit from considering previous works on the piloted ignition of heated solids [31-34]. Numerous studies on the piloted ignition of solids have shown that the ignition event occurs when the mass flux of pyrolysate reaches a critical value, allowing the mixture to surpass the lean flammability limit. Although practical limitations have prohibited measurement of the sample mass loss rate during experiments in this current study, it has been observed that the amount of visual smoke (pyrolysate) produced by the sample is strongly correlated to the piloted transition to flaming event. That is, it was observed that the amount of pyrolysate increases until a piloted transition to flaming occurs. This observation supports the concept of a lean flammability limit criterion for the piloted transition to flaming.

From the concept of a lean flammability limit criterion, it follows that the time delay between igniter activation and the piloted transition to flaming is the time needed for the smolder reaction to reach the critical rate of pyrolysate production. Before the piloted ignition event, the gaseous mixture is too lean to support a gas-phase ignition, due to insufficient pyrolysate concentration. Over time, the smolder reaction gradually intensifies, as can be seen by the increasing temperatures at 20 and 40 mm in Fig. 3, and the rate of pyrolysate production increases with time (as observed visually). When the gaseous mixture passing through the pilot passes the lean flammability limit, piloted ignition occurs.

The results in Table 1 show that increasing the oxygen concentration increases the likelihood of a piloted transition from smoldering to flaming, and generally decreases the time delay to transition. Increased oxygen concentration increases the smolder reaction rate, therefore increasing the heat generation and raising the temperature in the solid phase, which increases the rate of pyrolysate production. Therefore, increased oxygen concentration can cause the gaseous mixture to pass the lean flammability limit, and allow piloted transition to flaming. Similarly, increased oxygen concentration causes the smolder reaction to intensify more quickly, shortening the time delay to reach the critical rate of pyrolysate production.

Table 1 also shows that increasing the radiant heat flux increases the likelihood of a piloted transition from smoldering to flaming, and generally decreases the time delay to transition. Increased radiant heat flux raises the temperature in the solid phase, therefore directly increasing the rate of pyrolysate production. The increased radiant heat flux also increases the smolder reaction rate, further raising the solid-phase temperature and the rate of pyrolysate production. Therefore, increased radiant heat flux can cause the gaseous mixture to pass the lean flammability limit, and allow piloted transition to flaming. Similarly, increased radiant heat flux shortens the time delay to reach the critical rate of pyrolysate production.

Although Table 1 shows that increasing the oxygen concentration or increasing the radiant heat flux generally decreases the time delay to transition, there is interesting behavior for the tests at the highest oxygen mole fraction (0.35) and highest radiant heat flux (5.5 kW/m²). For these conditions, the time delay is longer than might be expected given the trends in the data. These tests were repeated to verify the results, and no significant difference was observed; the data reported is the average time delay for two tests. The cause of this unusual result is not known for certain. However, it was observed during these particular tests that the plume of smoke (pyrolysate) had a noticeably higher vertical velocity than that for other tests. It is possible that at these test conditions, the higher temperatures of the pyrolysate gas plume induce larger buoyant velocities. An increased vertical velocity of the pyrolysate would decrease the residence time through the pilot, which could inhibit gas-phase ignition due to Damkohler number (residence time vs. chemical time) limitations, and therefore cause a delay in piloted ignition. The transition to flaming could be delayed until the gas mixture has sufficient fuel to decrease the chemical time below the residence time. Another possibility is that the increased velocity of the gases reduces the time available for mixing of the fuel and oxidizer before they arrive at the pilot. Inadequate mixing would hinder gas-phase ignition. Lastly, it is also possible that higher oxygen concentrations and/or temperatures have different effects on the rates of release of gas-phase fire retardants and fuel from the foam.

Previous work on the spontaneous (unpiloted) transition to flaming found that high-density Pyrell could be ignited at lower oxygen concentrations and lower radiant heat fluxes than low-density Pyrell [19]. Although no differences have been found between the two Pyrell foams with respect to their limiting external conditions for the piloted transition to flaming, Table 1 does show that high-density Pyrell exhibits shorter time delays to transition than does low-density Pyrell. This result at least supports the previous observation that, in terms of their flammability behaviors, the high-density Pyrell is more hazardous than low-density Pyrell. In an effort to explain the differences in the time delay to transition, it is possible that the two foams have slightly different chemical compositions, which could affect their kinetic behavior in both the solid and gas phases. In addition, the differences in the microstructure of the two foams must account for some differences in flammability. As mentioned above, the high-density Pyrell has approximately 67% more solid surface area per unit volume of foam than the low-density Pyrell, which provides more locations for smoldering reactions to take place. As a result, high-density Pyrell can produce extra heat, and therefore can produce more gaseous fuel than low-density Pyrell, which would allow the gaseous mixture to pass the lean flammability limit at an earlier time.

4.1. Effects of Fire Retardants

A previous study by Putzeys et al. [18] used the same experimental configuration to examine the piloted transition from smoldering to flaming in a flexible non-fire retarded (NFR) polyurethane foam of density 26.5 kg/m³. Comparing the results of the experiments on NFR polyurethane foam to current results for Pyrell can help determine the effects of the fire retardants on the piloted transition from smoldering to flaming.

The fire retardants in Pyrell can have a two-fold effect on the piloted transition from smoldering to flaming. First, the fire retardants can act in the solid phase to hinder the smolder reaction. Pyrell could include melamine, for example, which is believed to act as a heat sink [27] and can form into thermally stable network structures [25]. As expected, this study has found that Pyrell requires significantly more external heat input in order to initiate a smolder reaction and allow a piloted transition to flaming. In the present study, the power of the igniter needed to be set significantly higher for Pyrell (115 W) than for the NFR foam (23 W) previously studied [10].

Secondly, the fire retardants in Pyrell can also hinder gas-phase reactions, which would further impede the piloted transition to flaming process. The fire retardants probably include halogen-phosphorus-containing additives that vaporize and inhibit gas-phase reactions in two ways: dilution of the volatile fuel mixture, and scavenging of OH* and H* radicals in the gas phase. In order to compensate for these fire retardant effects, it was necessary to raise the pilot current from 8.8 A (approximately 810 °C, as measured with an infrared camera) as used in the work on NFR foam, to 10 A (approximately 900 °C) for this study. This corresponds to a 30% increase in power supplied to the pilot. Increasing the pilot power causes the gas parcel passing through the pilot to be heated to a higher temperature, thereby increasing the gas-phase reaction rates and potentially overcoming the radical-scavenging and diluting effects of the fire retardants.

Finally, the fire retardants in Pyrell raised the threshold oxygen mole fraction for the piloted transition to flaming to 0.23, as opposed to 0.17 for NFR polyurethane foam. The elevated oxygen concentrations were necessary to generate more heat from smoldering, so as to produce more pyrolysate to overcome the fire retardant effects of dilution and radical scavenging. In addition, higher oxygen concentration can help overcome the gas-phase fire retardant effects by increasing the gas-phase oxidation reaction rates, enabling piloted ignition.

4.2. Comparison with the spontaneous transition from smoldering to flaming

A previous study by Putzeys et al. [19] used the same experimental configuration (minus the pilot) to investigate the spontaneous transition from smoldering to flaming in both low-density and high-density Pyrell. In contrast to the piloted transition to flaming, the spontaneous transition to flaming is an auto-ignition process in which the smoldering reaction acts the source of fuel and heat for gas-phase ignition. That study found that the spontaneous transition to flaming did not occur for oxygen mole fractions below 0.35 for high-density Pyrell, or under 0.40 for low-density Pyrell. However, the present work shows that piloted transition to flaming can occur in both low-density and high-density Pyrell in oxygen mole fractions as low as 0.23. The difference in the threshold oxygen concentrations is due to the fundamental difference in ignition mechanisms: the spontaneous transition to flaming depends on the gaseous mixture to generate sufficient heat on its own to undergo a thermal runaway (i.e. auto-ignition), rather than benefiting from the assistance of a pilot to provide the energy to initiate the gas-phase ignition. In the piloted transition to flaming, the pilot heats a small portion of the gas to a temperature

sufficient to initiate radical chain-branching reactions. In the spontaneous transition to flaming, the smolder reaction itself must raise the temperature of a gas parcel to a sufficient temperature to initiate a thermal runaway process, in which the concentration of radicals is coupled to the gas-phase temperature. The extra oxygen increases the heat generation of the smolder reaction, increasing the temperature in the gas parcels in the foam and allowing gas-phase auto-ignition. In addition, extra oxygen increases the gas-phase reaction rates, facilitating the auto-ignition process.

5. Conclusion

The piloted transition from smoldering to flaming, though a significant fire safety concern, has not been previously extensively studied. The present experiments show that the piloted transition from smoldering to flaming in Pyrell is possible under a wider range of external conditions than the spontaneous transition from smoldering to flaming. Therefore, in the presence of a high temperature heat source that can act as a pilot (i.e. spark, hot spot, etc.), the piloted transition to flaming presents a significantly greater risk than the spontaneous transition to flaming.

The experiments indicate that the piloted transition from smoldering to flaming occurs when the gaseous mixture at the pilot passes the lean flammability limit. Increasing the oxygen concentration or the external heat flux increases the likelihood of a piloted transition from smoldering to flaming, and generally decreases the time delay to transition. In addition, it was found that high-density Pyrell undergoes a piloted transition from smoldering to flaming more quickly than low-density Pyrell. A possible explanation is that the high-density Pyrell has more solid surface area for smoldering reactions to take place, thus producing more heat and gaseous fuel, which allows a passing of the lean flammability limit at an earlier time.

The fire retardants in Pyrell can act in both the solid phase and the gas phase to hinder the piloted transition from smoldering to flaming. In order to compensate for the effects of the fire retardants on the piloted transition from smoldering to flaming in Pyrell, it was necessary to raise the igniter power and the pilot power relative to the values used for NFR foam, and to raise the oxygen concentration to above-ambient values.

In summary, these experiments have shown that the fire retardants in Pyrell are quite effective in preventing the piloted transition from smoldering to flaming in normal air. However, the results show that Pyrell is susceptible to smoldering and the piloted transition to flaming in oxygen-enriched environments as low as 23% oxygen. Considering NASA's plans for using elevated oxygen concentrations for future space missions, there should be concern about the behavior of Pyrell in such conditions. Precautions should be taken in the design of applications of Pyrell in oxygen-enriched environments to reduce to the risk of a fire in spacecraft and space habitats. The results of this study indicate that in oxygen-enriched environments, it is critical to minimize the exposure of Pyrell to any potential high-temperature heat sources to prevent a piloted transition to flaming.

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